

plane is 1.566 Å. The vector O(W)—O(9) is inclined to this plane by 34.8°. O(W) is out of the C(1'), C(2'), O(9'), O(10') least-squares plane by a perpendicular distance of 2.090 Å, and the angle of inclination of the O(W)—O(10') vector to this plane is 47.7°. In their recent survey of OH...O hydrogen-bond geometries, Mitra & Ramakrishnan (1977) report that angles of inclination in the range 30–50° were found in only 12 out of 77 cases involving hydrogen bonds to carbonyl groups.

The two pyrrolidine rings have different conformations which can be described quite successfully using the conformational equations of DeTar & Luthra (1977). According to these authors, the *i*th torsional angle in a five-membered ring is given by the equation

$$\chi_i = a_o \cos [t + 4\pi(i - 2)/5], \quad (1)$$

where  $a_o$  is the puckering amplitude and  $t$  is a phase angle. Envelope conformations occur when  $t = 18, 54^\circ$ , etc., while half-chair conformations occur when  $t = 0, 36, 72^\circ$ , etc. DeTar & Luthra have tabulated the values of  $a_o$ ,  $t$ , and the additional parameter  $d_1 = (\chi_3 - \chi_2)/2$ , for the pyrrolidine rings in 40 proline derivatives.

In the present instance the 'primed' pyrrolidine ring has  $a_o = 41.3^\circ$ ,  $t = 17.0^\circ$ , and  $d_1 = -7.1^\circ$ . It is an almost perfect envelope with C(7') as the flap. The other four atoms in the ring are coplanar to within  $\pm 0.004$  Å, with C(7') out of the plane by 0.60 Å on the same side as H(4').

The pyrrolidine ring in the 'unprimed' conformer, with parameters  $a_o = 43.4^\circ$ ,  $t = 46.3^\circ$ , and  $d_1 = -18.45^\circ$ , is relatively unusual in that the most puckered center is a C atom bonded to the N. This behavior was shown by only two of the 40 rings characterized by DeTar & Luthra. C(8) is 0.51 Å out of the N(4), C(5), C(6) plane, on the same side as C(3), while C(7) is only 0.15 Å out of this plane on the opposite side.

#### References

- DE TAR, D. F. & LUTHRA, N. P. (1977). *J. Am. Chem. Soc.* **99**, 1232–1244.  
 DONOHUE, J. (1968). *Structural Chemistry and Molecular Biology*, edited by A. RICH & N. DAVIDSON, pp. 443–465. San Francisco: Freeman.  
 HOPE, H. (1971). *J. Appl. Cryst.* **4**, 333.  
 HORSMA, D. A. & NASH, C. P. (1968). *J. Phys. Chem.* **72**, 2351–2358.  
 JOHNSON, C. K. (1970). *ORTEP*. Report ORNL-3794, 2nd revision. Oak Ridge National Laboratory, Tennessee.  
 KOETZLE, T. F. & LEHMANN, M. S. (1976). *The Hydrogen Bond*, Vol. II, edited by P. SCHUSTER, G. ZUNDEL & C. SANDORFY, pp. 457–469. Amsterdam: North-Holland.  
 LONG, R. E. (1965). PhD dissertation. Univ. of California, Los Angeles.  
 MITRA, J. & RAMAKRISHNAN, C. (1977). *Int. J. Pept. Protein Res.* **9**, 27–48.  
 PETERSON, M. A., HOPE, H. & NASH, C. P. (1979). *J. Am. Chem. Soc.* **101**, 946–950.  
 SAYRE, D. (1952). *Acta Cryst.* **5**, 60–65.

*Acta Cryst.* (1982). **B38**, 2493–2496

### *N*-(*o*-Bromophenyl)-*o*-bromobenzylamine

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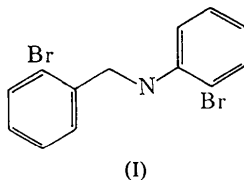
(Received 6 October 1981; accepted 30 March 1982)

**Abstract.** C<sub>13</sub>H<sub>11</sub>Br<sub>2</sub>N,  $M_r = 341.06$ , triclinic,  $P\bar{1}$ ,  $a = 10.930$  (2),  $b = 11.291$  (9),  $c = 10.749$  (2) Å,  $\alpha = 108.10$  (3),  $\beta = 92.83$  (2),  $\gamma = 85.25$  (4)°,  $V = 1256$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.803$  g cm<sup>-3</sup>. The structure was solved by heavy-atom techniques and refined by least squares, using 2241 observed data with  $F_o > 3\sigma(F_o)$ , and anisotropic temperature factors, to  $R_w = 0.031$  and  $R = 0.044$ . The two halves of each of the two molecules in the asymmetric unit are rotated about

the central C—N bond to make dihedral angles of 79.0 and 76.9°. The average Br—C distance is 1.894 (8) Å and the average C—C (ring) distance is 1.379 (12) Å.

**Introduction.** Many tricyclic compounds show psychotropic activity (Chang, 1979). Useful precursors to these potential drugs contain *o*-bromo-substituted phenyl rings separated by one or more atoms (Chang, 1979). These latter materials provide a vehicle for the

study of the effects of intramolecular interactions on the configuration about the central atoms, and they have been the subject of several investigations (Corey, 1979, and references therein; Berndt, Corey & Glick, 1981). To extend these studies the structure of the title compound (I) was investigated.



**Experimental.** Crystals were prepared by Chang (1979). A small crystal of the title compound, approximately  $0.1 \times 0.13 \times 0.3$  mm, was mounted with random orientation on an Enraf-Nonius CAD-4 diffractometer for data collection. 25 carefully centered reflections were used to obtain the orientation matrix and unit-cell dimensions. The Delaunay reduced unit cell was found to be triclinic. The intensities of 3340 reflections were measured by the  $\theta$ - $2\theta$  step-scan technique (Mo  $K\alpha$  radiation, graphite monochromator) with  $2\theta < 45^\circ$ . Three standard reflections were used to check crystal orientation after every 200 reflections, and the 25 original reflections were re-centered and used to calculate a new orientation matrix when the standards were found to be significantly off-center. In addition, the intensities of three standard reflections were measured after every 8000 s of X-ray exposure to check on crystal and X-ray-beam stability. These showed no significant change during the entire data-collection process.

Equivalent reflections were measured to yield 3161 unique reflections of which the 2241 data with  $F_o > 3\sigma(F_o)$  were used in the structure solution and refinement. The data were corrected for absorption using the empirical  $\psi$ -scan method ( $\mu = 68.1 \text{ cm}^{-1}$ ; transmission factors: minimum 0.886, maximum 1.00, average = 0.957).

The structure was determined by heavy-atom techniques and was refined by the least-squares method (Busing, Martin & Levy, 1962). The scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Real and imaginary anomalous-dispersion corrections were made for the Br atoms. No correction was applied for extinction.

There are two molecules in the asymmetric unit. The positional coordinates of the Br atoms were determined from a Patterson map and the remaining non-hydrogen atoms were located from an electron density map calculated with phases determined by the Br atoms. Refinement was completed with anisotropic temperature factors and inclusion of H atoms at fixed positions (Zalkin, 1974) with  $B = 5.0 \text{ \AA}^2$ . The H atoms

were relocated after each cycle of refinement with C—H and N—H distances of 1.0 Å. A total of 289 parameters were refined. The largest positional-parameter and temperature-factor shifts in the final cycle of refinement were  $0.61\sigma$  and  $0.39\sigma$ , respectively. The final value of  $R_w = \{[\sum w(F_o - |F_c|)^2]^{1/2} / (\sum wF_o^2)^{1/2}\}$  was 0.031 and the final value of  $R = (\sum ||F_o| - |F_c|| / \sum |F_o|)$  was 0.044. The largest peak in the final difference map was  $0.87 \text{ e \AA}^{-3}$ , in the vicinity of Br(3).

**Discussion.** The final atomic parameters for all non-hydrogen atoms are given in Table 1. All atoms are in the general position. The numbers in parentheses are the standard deviations in the least significant figure as estimated from the least-squares analysis.\* A perspective drawing of one molecule illustrating the

\* Lists of structure factors, final H-atom positions and anisotropic temperature factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36833 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic positional parameters ( $\times 10^4$ ) and equivalent isotropic thermal parameters for the nonhydrogen atoms

$$B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j \text{ (Hamilton, 1959).}$$

	x	y	z	$B_{eq} (\text{\AA}^2)$
Br(1)	9010 (1)	6829 (1)	9013 (1)	6.59
Br(2)	2375 (1)	5311 (1)	8620 (1)	5.48
Br(3)	9529 (1)	3201 (1)	7736 (1)	6.61
Br(4)	7590 (1)	1040 (1)	562 (1)	9.37
C(11)	8209 (7)	6168 (6)	7377 (7)	4.00
C(12)	8814 (7)	6078 (7)	6255 (9)	5.01
C(13)	8259 (8)	5597 (8)	5041 (8)	5.54
C(14)	7103 (7)	5168 (7)	4963 (7)	4.29
C(15)	6514 (6)	5226 (7)	6090 (7)	3.91
C(16)	7048 (6)	5734 (6)	7315 (7)	3.44
N(1)	6446 (6)	5812 (6)	8494 (6)	5.37
C(21)	3643 (7)	4005 (7)	8196 (7)	3.96
C(22)	3340 (7)	2780 (8)	7951 (8)	5.28
C(23)	4245 (9)	1841 (8)	7686 (9)	5.90
C(24)	5440 (8)	2103 (8)	7685 (8)	5.63
C(25)	5738 (7)	3324 (8)	7912 (7)	4.75
C(26)	4846 (7)	4307 (7)	8179 (6)	3.78
C(27)	5150 (6)	5591 (7)	8430 (6)	3.86
C(31)	9034 (6)	1567 (7)	6867 (9)	4.74
C(32)	9153 (7)	717 (11)	7562 (9)	6.30
C(33)	8826 (9)	-481 (10)	6966 (12)	7.04
C(34)	8385 (8)	-803 (8)	5682 (12)	6.61
C(35)	8275 (7)	49 (9)	5005 (8)	5.35
C(36)	8585 (6)	1286 (8)	5585 (9)	4.38
N(3)	8504 (6)	2193 (6)	4923 (7)	6.21
C(41)	6441 (8)	1372 (7)	1908 (8)	5.03
C(42)	5214 (10)	1267 (8)	1559 (10)	6.65
C(43)	4361 (9)	1451 (9)	2500 (13)	7.40
C(44)	4738 (8)	1757 (8)	3770 (11)	6.54
C(45)	5951 (8)	1892 (7)	4126 (8)	5.21
C(46)	6841 (7)	1703 (7)	3192 (8)	4.12
C(47)	8146 (7)	1825 (7)	3549 (8)	4.41

Table 2. *Interatomic distances (Å) and angles (°)*

Br(1)—C(11)	1.885 (7)	Br(3)—C(31)	1.901 (8)
C(11)—C(12)	1.377 (12)	C(31)—C(32)	1.384 (16)
C(12)—C(13)	1.379 (12)	C(32)—C(33)	1.374 (15)
C(13)—C(14)	1.380 (12)	C(33)—C(34)	1.387 (17)
C(14)—C(15)	1.382 (11)	C(34)—C(35)	1.369 (17)
C(15)—C(16)	1.383 (10)	C(35)—C(36)	1.404 (12)
C(16)—C(11)	1.389 (10)	C(36)—C(31)	1.388 (13)
C(16)—N(1)	1.433 (10)	C(36)—N(3)	1.412 (13)
Br(2)—C(21)	1.900 (7)	Br(4)—C(41)	1.891 (9)
C(21)—C(22)	1.391 (13)	C(41)—C(42)	1.379 (14)
C(22)—C(23)	1.361 (12)	C(42)—C(43)	1.366 (17)
C(23)—C(24)	1.363 (14)	C(43)—C(44)	1.352 (17)
C(24)—C(25)	1.387 (13)	C(44)—C(45)	1.369 (12)
C(25)—C(26)	1.385 (11)	C(45)—C(46)	1.389 (12)
C(26)—C(21)	1.387 (11)	C(46)—C(41)	1.372 (12)
C(26)—C(27)	1.454 (11)	C(46)—C(47)	1.465 (10)
C(27)—N(1)	1.453 (10)	C(47)—N(3)	1.448 (11)
Average C—C (ring)	1.379 (12)	Average Br—C	1.894 (8)
Br(1)—C(11)—C(12)	118.9 (5)	Br(3)—C(31)—C(32)	117.2 (6)
Br(1)—C(11)—C(16)	120.1 (6)	Br(3)—C(31)—C(36)	119.2 (7)
C(16)—C(11)—C(12)	121.0 (7)	C(36)—C(31)—C(32)	123.7 (8)
C(11)—C(12)—C(13)	120.6 (7)	C(31)—C(32)—C(33)	119.2 (9)
C(12)—C(13)—C(14)	119.1 (8)	C(32)—C(33)—C(34)	118.9 (12)
C(13)—C(14)—C(15)	120.1 (7)	C(33)—C(34)—C(35)	121.2 (9)
C(14)—C(15)—C(16)	121.3 (7)	C(34)—C(35)—C(36)	121.6 (8)
C(15)—C(16)—C(11)	117.9 (7)	C(35)—C(36)—C(31)	115.4 (9)
C(11)—C(16)—N(1)	120.1 (6)	C(31)—C(36)—N(3)	120.8 (7)
C(15)—C(16)—N(1)	122.1 (6)	C(35)—C(36)—N(3)	123.7 (8)
C(16)—N(1)—C(27)	119.1 (6)	C(36)—N(3)—C(47)	118.9 (6)
Br(2)—C(21)—C(22)	118.9 (6)	Br(4)—C(41)—C(42)	118.3 (7)
Br(2)—C(21)—C(26)	118.9 (6)	Br(4)—C(41)—C(46)	119.8 (7)
C(26)—C(21)—C(22)	122.2 (7)	C(46)—C(41)—C(42)	121.9 (8)
C(21)—C(22)—C(23)	119.4 (8)	C(41)—C(42)—C(43)	120.0 (9)
C(22)—C(23)—C(24)	120.2 (8)	C(42)—C(43)—C(44)	119.0 (9)
C(23)—C(24)—C(25)	120.3 (8)	C(43)—C(44)—C(45)	121.3 (10)
C(24)—C(25)—C(26)	121.4 (8)	C(44)—C(45)—C(46)	121.1 (8)
C(25)—C(26)—C(21)	116.6 (8)	C(45)—C(46)—C(41)	116.6 (7)
C(21)—C(26)—C(27)	121.6 (7)	C(41)—C(46)—C(47)	121.3 (8)
C(25)—C(26)—C(27)	121.8 (7)	C(45)—C(46)—C(47)	122.0 (7)
C(26)—C(27)—N(1)	116.9 (6)	C(46)—C(47)—N(3)	118.5 (7)

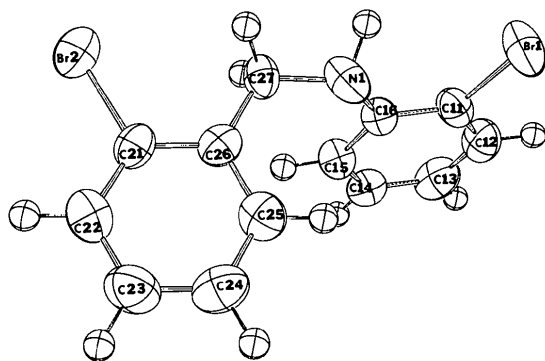


Fig. 1. A perspective drawing of one molecule of (I), showing the atom-numbering scheme used. The atom-numbering scheme for the second molecule was obtained by replacing the numeral 1 by 3 and the numeral 2 by 4 when they appear as the first (or only) numeral in the atom identification.

atom-numbering scheme used is given in Fig. 1 (Johnson, 1965). Bond distances and angles and their estimated standard deviations (Busing, Martin & Levy, 1964) are given in Table 2.

The two halves of the molecules are approximately perpendicular. In the molecule defined by rings (1) and (2) the angle between the normals to the planes of the two phenyl moieties is  $79.0^\circ$  while in the molecule defined by rings (3) and (4) this angle is  $76.9^\circ$ . The largest displacement of an atom from the best plane of a phenyl moiety is  $0.038 \text{ \AA}$  for C(42). The shortest intermolecular distance that involves a nonhydrogen atom and an H atom is  $2.840 \text{ \AA}$ . The shortest intermolecular distance between non-hydrogen atoms is  $3.367 \text{ \AA}$ , and the shortest intermolecular  $\text{H}\cdots\text{H}$  distance is  $2.336 \text{ \AA}$ .

The average C(ring)—N distance is  $1.422 (8) \text{ \AA}$  while the central C—N distance is  $1.450 (7) \text{ \AA}$ . These values are slightly smaller than the sum of the single-bond radii,  $1.47 \text{ \AA}$  (Pauling, 1960), suggesting that these bonds have some double-bond character. The comparable C(ring)—N distance in aniline derivatives lies between  $1.437 (13)$  and  $1.483 (15) \text{ \AA}$  (Van Bellingen, Germain, Piret & Van Meerssche, 1971*a, b*; Hulme & Scruton, 1968).

In dibenzyl and related compounds the phenyl rings lie in parallel planes approximately perpendicular to the best plane of the central bonds of the molecule (observed angles  $72\text{--}89^\circ$ ; Corey, 1979). In the title compound the observed configuration, which results from rotation of a planar molecule about the C—N central bond, is probably favored because of interactions with the amine H and/or the lone pair of N electrons.

The compound *o*-bromobenzyl *o*-bromophenyl ether is isoelectronic with the title compound. Preliminary structural studies, in this laboratory, on the ether suggest that this molecule is approximately planar with the two Br atoms lying on opposite sides of the molecule as opposed to the nearly perpendicular configuration observed for the amine. The reason for the difference appears to lie in the symmetry of the two lone pairs of O electrons which does not favor rotation about the C—O central bond.

One of us (AFB) is grateful to the Research Committee of the University of Missouri—St Louis for financial support through a Summer Research Fellowship.

#### References

- BERNDT, A. F., COREY, E. R. & GLICK, M. D. (1981). *Acta Cryst.* **B37**, 1294–1296.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE*. Report ORNL-TM-306. Oak Ridge National Laboratory, Tennessee.
- CHANG, V. H. T. (1979). *Syntheses of Some Tricyclic Compounds Containing Oxygen and Silicon Heteroatoms*. MS Thesis, Univ. of Missouri—St Louis.

COREY, E. R. (1979). *Acta Cryst.* **B35**, 201–203.  
 HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.  
 HULME, R. & SCRUTON, J. C. (1968). *J. Chem. Soc. A*, pp. 2448–2452.  
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.  
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed., p. 224. Ithaca: Cornell Univ. Press.  
 VAN BELLINGEN, I., GERMAIN, G., PIRET, P. & VAN MEERSSCHE, M. (1971a). *Acta Cryst.* **B27**, 553–559.  
 VAN BELLINGEN, I., GERMAIN, G., PIRET, P. & VAN MEERSSCHE, M. (1971b). *Acta Cryst.* **B27**, 560–564.  
 ZALKIN, A. (1974). *A FORTRAN Program for the Calculation of Idealized Hydrogen Positions*. Univ. of California, Berkeley. (Local program version.)

*Acta Cryst.* (1982). **B38**, 2496–2498

## Structure of 7,8-Dihydro-4,7,7-trimethyl-2*H*,5*H*-pyrano[4,3-*b*]pyran-2,5-dione

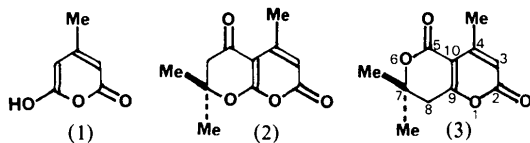
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(Received 8 February 1982; accepted 1 April 1982)

**Abstract.** C<sub>11</sub>H<sub>12</sub>O<sub>4</sub>, *M<sub>r</sub>* = 208.2, monoclinic, *P*2<sub>1</sub>/*c*, *Z* = 4, *a* = 11.908 (5), *b* = 9.611 (4), *c* = 9.437 (6) Å, β = 107.99 (5)°, *V* = 1027.2 Å<sup>3</sup>, *D<sub>x</sub>* = 1.35, *D<sub>m</sub>* = 1.34 (1) g cm<sup>-3</sup>; Mo *K*α radiation, μ = 1.11 cm<sup>-1</sup>, λ = 0.71073 Å. Final *R* = 0.043 for 1095 observations. The structure consists of one crystallographically independent molecule separated from its neighbors by ordinary van der Waals distances. The structure of the title compound was not the expected dimerization product.

**Introduction.** In the course of a reaction with 6-hydroxy-4-methyl-2-pyrone (1) (Bland & Thorpe, 1912) a dimerization occurred to yield a crystalline product, m.p. 426 K, which was thought to be (2) or (3). The preparation is described by Burke, Saunders & Murtiashaw (1981). Mechanistic and spectroscopic evidence favored structure (2), but (3) could not be eliminated. The structure analysis was undertaken to settle this issue.



The ring-closure product (2) or (3) was prepared as described by Burke *et al.* (1981). The crystals were grown from a hexane–ether solution over a period of two weeks. A single parallelepiped-shaped crystal of ~0.31 × 0.07 × 0.08 mm was mounted on a glass fiber on a goniometer head on a CAD-4 diffractometer

Table 1. *Data collection and refinement parameters*

Graphite monochromator  
 Faces: (010), (0 $\bar{1}$ 0), ( $\bar{1}$ 00), (110), (011), (0 $\bar{1}$  $\bar{1}$ )  
 Absorption corrections made and max./min. transmission factors found were 0.997–0.985 (Frenz, 1980)  
*P* factor = 0.030 in  $\sigma(F_o^2) = [\sigma(I_{\text{raw}})^2 + (P \times I_{\text{raw}})^2]^{1/2}/Lp$  and  $w = 1/\sigma(F_o)^2$   
 Data considered non-zero if  $F^2 > 4\sigma(F^2)$   
 4509 independent *hkl*'s measured in  $\omega$ -2 $\theta$  mode  
 1095 reflections used to solve and refine structure (data collection could have been terminated at lower 2 $\theta$ )  
 Three standard reflections monitored every 100 reflections, decay less than 2% *I*  
 Room temperature ~291 K  
 Structure refined by full-matrix least squares, including anisotropic temperature factors and anomalous-dispersion corrections with weights based upon intensity statistics (Frenz, 1980); function refined was  $\sum_i w_i (|F_o| - |F_c|)^2$   
 Final least squares performed on Amdahl V6 with weights as per option 5 and *F<sub>min</sub>* = 3.5 (Stewart, 1979)  
 Final *R* = 0.043, weighted *R* = 0.052  
 Error of observation of unit weight = 1.55

interfaced to a PDP-11/40 computer. The crystal was aligned and intensity data were collected by standard techniques (Enraf–Nonius, 1980). Details are found in Table 1.

The structure was solved with direct methods *via MULTAN 78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978; Main, 1976) in which the overall molecular geometry was utilized to generate starting phases. Without the molecular geometry, the phase sets generated *E* maps of continuous hexagonal geometry in which the structure was not readily apparent regardless of various levels of sin  $\theta$  data truncations. Refinement was by full-matrix least squares

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